

What is claimed is:

1. A porous microcomposite comprising perfluorinated ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight
5 percentage of perfluorinated ion-exchange polymer in the microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the microcomposite is about 0.5 nm to about 75 nm, and wherein the microcomposite optionally further comprises pores having a size in the range of about 75 nm to about 1000 nm.
- 10 2. The microcomposite of Claim 1 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups.
3. The microcomposite of Claim 1 wherein the metal oxide is silica, alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic oxide and/or iron oxide.
- 15 4. The microcomposite of Claim 1 wherein the metal oxide is silica.
5. The microcomposite of Claim 4 wherein the perfluorinated ion-exchange polymer is prepared from resin having an equivalent weight of about 1070 comprising about 6.3 tetrafluoroethylene molecules for every
20 perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl fluoride) molecule, and the weight percent of perfluorinated ion-exchange polymer is about 13%.
6. The microcomposite of Claim 1 wherein the weight percentage of perfluorinated ion-exchange polymer is from about 5 to about 80.
7. The microcomposite of Claim 1 wherein the size of the pores is about 0.5 nm to about 30 nm.
- 25 8. The microcomposite of Claim 1 wherein said microcomposite further comprises pores having a size in the range of about 75 nm to about 1000 nm.
9. The microcomposite of Claim 8 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups, and wherein the metal
30 oxide is silica.
10. The process of preparation of a porous microcomposite which comprises perfluorinated ion-exchange polymer containing pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight percentage of perfluorinated ion-
35 exchange polymer in the microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the microcomposite is about 0.5 nm to about 75 nm, and wherein the microcomposite optionally further comprises pores having a size in the range of about 75 nm to about 1000 nm;

- said process comprising the steps of:
- a. mixing the perfluorinated ion-exchange polymer with one or more metal oxide precursors in a common solvent;
 - b. initiating gelation;
 - c. allowing sufficient time for gelation and aging of the mixture; and
 - d. removing the solvent.
11. The process of Claim 10 further comprising the steps, after d:
- e. acidifying the product of step d by addition of an acid;
- 10 and
- f. removing the excess acid.
12. The process of Claim 11 further comprising at step a, adding to the mixture an amount from about 1 to 80 weight percent of an acid extractable filler particle, whereby said microcomposite further contains pores having a size
- 15 in the range of about 75 nm to about 1000 nm.
13. The process of Claim 12 wherein the acid extractable filler particle is calcium carbonate.
14. The process of Claim 10 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups.
- 20 15. The process of Claim 10 wherein the metal oxide is silica.
16. The process of Claim 11 further comprising after step d and before step e: grinding the product of step d.
17. An improved process for the nitration of an aromatic compound wherein the improvement comprises contacting said aromatic compound with a
- 25 catalytic porous microcomposite comprising perfluorinated ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight percentage of perfluorinated ion-exchange polymer in the microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the
- 30 microcomposite is about 0.5 nm to about 75 nm, and wherein the microcomposite optionally further comprises pores having a size in the range of about 75 nm to about 1000 nm.
18. The process of Claim 17 wherein the aromatic compound is benzene.
- 35 19. The process of Claim 17 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups and the metal oxide is silica, alumina, titania, germania, zirconia, aluminosilicate, zirconyl-silicate, chromic oxide and/or iron oxide.

20. The process of Claim 19 wherein the metal oxide is silica and said microcomposite further comprises pores having a size in the range of about 75 nm to about 1000 nm.

21. An improved process for the esterification of a carboxylic acid
5 with an olefin wherein the improvement comprises contacting said carboxylic acid with a catalytic porous microcomposite comprising perfluorinated ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight percentage of perfluorinated ion-exchange polymer in the
10 microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the microcomposite is about 0.5 nm to about 75 nm, and wherein the microcomposite optionally further comprises pores having a size in the range of about 75 nm to about 1000 nm.

22. The process of Claim 21 wherein the carboxylic acid is acetic
15 acid and the olefin is cyclohexene.

23. The process of Claim 21 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups and the metal oxide is silica, alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic oxide and/or iron oxide.

24. The process of Claim 23 wherein the metal oxide is silica and
20 said microcomposite further comprises pores having a size in the range of about 75 nm to about 1000 nm.

25. A process for regenerating a catalyst comprising perfluorinated ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups
25 entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight percentage of perfluorinated ion-exchange polymer in the microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the microcomposite is about 1 nm to about 75 nm, and wherein the microcomposite optionally further comprises pores having a size in the range of
30 about 75 nm to about 1000 nm, comprising the steps of:

- (a) contacting the microcomposite with an acid; and
- (b) removing the excess acid to yield the regenerated catalyst.

26. The process of Claim 25 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups and the metal oxide is silica,
35 alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic oxide and/or iron oxide.

27. The process of Claim 26 wherein the metal oxide is silica and said microcomposite further comprises pores having a size in the range of about 75 nm to about 1000 nm.

28. An improved process for the dimerization of an alpha substituted
5 styrene wherein the improvement comprises contacting said alpha substituted
styrene with a catalytic porous microcomposite comprising perfluorinated ion-
exchange polymer with pendant sulfonic and/or carboxylic acid groups
entrapped within and highly dispersed throughout a network of metal oxide,
wherein the weight percentage of perfluorinated ion-exchange polymer in the
10 microcomposite is from about 0.1 to about 90 percent, wherein the size of the
pores in the microcomposite is about 1 nm to about 75 nm, and wherein the
microcomposite optionally further comprises pores having a size in the range of
about 75 nm to about 1000 nm.

29. The process of Claim 28 wherein the alpha substituted styrene is
15 alpha methyl styrene.

30. The process of Claim 28 wherein the perfluorinated ion-exchange
polymer contains pendant sulfonic acid groups and the metal oxide is silica,
alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic
oxide and/or iron oxide.

20 31. The process of Claim 30 wherein the metal oxide is silica and
said microcomposite further comprises pores having a size in the range of about
75 nm to about 1000 nm.

32. An improved process for the alkylation of an aromatic compound
with an olefin wherein the improvement comprises contacting said aromatic
25 compound with ^{and the olefin} a catalytic porous microcomposite comprising perfluorinated
ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups
entrapped within and highly dispersed throughout a network of metal oxide,
wherein the weight percentage of perfluorinated ion-exchange polymer in the
microcomposite is from about 0.1 to about 90 percent, wherein the size of the
30 pores in the microcomposite is about 1 nm to about 75 nm, and wherein the
microcomposite optionally further comprises pores having a size in the range of
about 75 nm to about 1000 nm.

33. The process of Claim 32 wherein the perfluorinated ion-exchange
polymer contains pendant sulfonic acid groups and the metal ^{or metalloid} oxide is silica,
35 alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic
oxide and/or iron oxide.

34. The process of Claim 33 wherein the metal oxide is silica and said microcomposite further comprises pores having a size in the range of about 75 nm to about 1000 nm.

35. An improved process for the polymerization of tetrahydrofuran to polytetramethylene ether acetate wherein the improvement comprises contacting said tetrahydrofuran with a catalytic porous microcomposite comprising perfluorinated ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight percentage of perfluorinated ion-exchange polymer in the microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the microcomposite is about 0.5 nm to about 75 nm; and wherein the microcomposite optionally further comprises pores having a size in the range of about 75 nm to about 1000 nm.

36. The process of Claim 35 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups and the metal oxide is silica, alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic oxide and/or iron oxide.

37. The process of Claim 36 wherein the metal oxide is silica and said microcomposite further comprises pores having a size in the range of about 75 nm to about 1000 nm.

38. An improved process for the acylation of an aromatic compound with an acyl halide wherein the improvement comprises contacting said aromatic compound with a catalytic porous microcomposite comprising perfluorinated ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight percentage of perfluorinated ion-exchange polymer in the microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the microcomposite is about 0.5 nm to about 75 nm, and wherein the microcomposite optionally further comprises pores having a size in the range of about 75 nm to about 1000 nm.

39. The process of Claim 38 wherein the aromatic compound is m-xylene and the acyl halide is benzoyl chloride.

40. The process of Claim 38 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups and the metal oxide is silica, alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic oxide and/or iron oxide.

41. The process of Claim 40 wherein the metal oxide is silica and said microcomposite further comprises pores having a size in the range of about 75 nm to about 1000 nm.

42. A process for the isomerization of an olefin, comprising
5 contacting said olefin at isomerization conditions with a catalytic amount of a porous microcomposite, said microcomposite comprising a perfluorinated ion-exchange polymer with pendant sulfonic and/or carboxylic acid groups entrapped within and highly dispersed throughout a network of metal oxide, wherein the weight percentage of perfluorinated ion-exchange polymer in the
10 microcomposite is from about 0.1 to about 90 percent, wherein the size of the pores in the microcomposite is about 0.5 nm to about 75 nm, and wherein the microcomposite optionally further comprises pores having a size in the range of about 75 nm to about 1000 nm.

43. The process of Claim 42 wherein the isomerization conditions
15 comprise a temperature of from about 0°C to about 300°C, a pressure of from about atmospheric to 100 atmospheres, and a weight hourly space velocity of from about 0.1 to 100 hr⁻¹.

44. The process of Claim 43 wherein the isomerization conditions
20 comprise a temperature of from about 25°C to about 250°C, a pressure of from about atmospheric to 50 atmospheres, and a weight hourly space velocity of from about 0.1 to 10 hr⁻¹.

45. The process of Claim 42 wherein the perfluorinated ion-exchange polymer contains pendant sulfonic acid groups.

46. The process of Claim 42 wherein the metal oxide is silica,
25 alumina, titania, germania, zirconia, alumino-silicate, zirconyl-silicate, chromic oxide and/or iron oxide.

47. The process of Claim 45 wherein the metal oxide is silica.

48. The process of Claim 42 wherein the weight percentage of perfluorinated ion-exchange polymer is from about 5 to about 80.

30 49. The process of Claim 48 wherein the weight percentage of perfluorinated ion-exchange polymer is from about 5 to about 20.

50. The process of Claim 42 wherein the size of the pores is about 0.5 nm to about 30 nm.

51. The process of Claim 42 wherein said microcomposite further
35 comprises pores having a size in the range of about 75 nm to about 1000 nm.

52. The process of Claim 42 wherein the olefin is a C₄ to C₄₀ primary olefin.

53. The process of Claim 52 wherein the olefin is 1-butene, 1-heptene or 1-dodecene.

54. The process of Claim 53 wherein the olefin is 1-butene.

55. The process of Claim 53 wherein the weight percentage of
5 perfluorinated ion-exchange polymer is from about 5 to about 80, the
perfluorinated ion-exchange polymer contains pendant sulfonic acid groups, and
the metal oxide is silica.

56. The process of Claim 53 wherein the perfluorinated ion-exchange
polymer is prepared from resin having an equivalent weight of about 1070
10 comprising about 6.3 tetrafluoroethylene molecules for every perfluoro (3,6-
dioxo-4-methyl-7-octenesulfonyl fluoride) molecule, and the weight percent of
perfluorinated ion-exchange polymer is about 13%.